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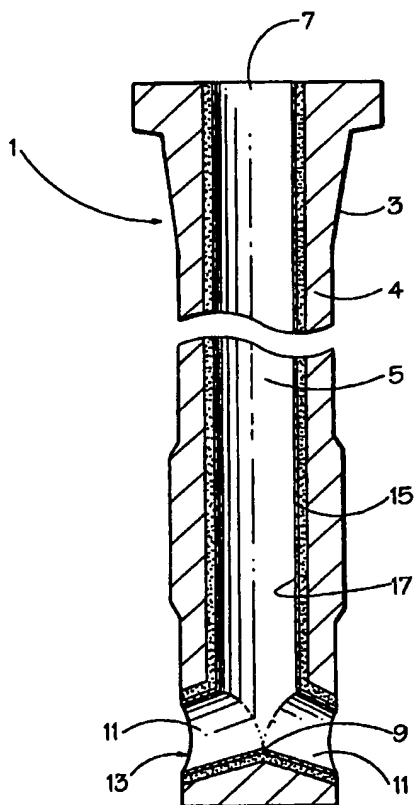
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(54) Title: ARTICLE FORMED FROM CARBON-BONDED REFRACTORY MATERIAL



(57) Abstract: An article (1), for example a nozzle or shroud, or a stopper rod, for use with molten metal, especially molten steel, comprising a body (3) formed from carbon-bonded refractory material (4), a surface layer (15) of the body being porous, the porous surface layer having a coating of glaze (17).

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Article Formed From Carbon-Bonded Refractory Material

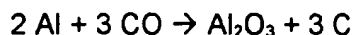
The present invention relates to the handling and control of molten metal by means of articles formed from carbon-bonded refractory material. The invention is particularly applicable to the continuous casting of steel, and to carbon-bonded refractory articles such as submerged pouring nozzles (commonly referred to as submerged entry nozzles or "SEN's"), ladle shrouds, stopper rods and the like, which are used in the continuous casting process.

During the manufacture of steel, oxygen normally becomes dissolved in the molten metal. In order to remove the dissolved oxygen from the steel, it is often "killed" by the addition of aluminium which reacts with the oxygen to form aluminium oxide (alumina). Some of the alumina floats to the surface of the steel and is removed with the slag, but some of it remains dispersed within the molten steel. The alumina which remains dispersed in the steel tends to become deposited on the carbon-bonded refractory articles such as submerged entry nozzles during the continuous casting process. This is a major problem because the build-up of alumina in the bore of a sub-entry nozzle reduces the rate of flow of the molten steel and necessitates frequent nozzle changes, thus shortening the duration of continuous casting cycles.

United States Patent No. 5,370,370 discloses a carbon-bonded refractory body, e.g. a submerged entry nozzle, having a metal contacting surface resistant to alumina build-up, the surface consisting of a carbon-free, oxidized zone formed in the surface and a carbon-free refractory material infiltrated into the carbon-free oxidized zone. The carbon-free refractory material is preferably alumina, silica, zirconia or SiAlON. The submerged entry nozzle or other carbon-bonded refractory body is manufactured as follows. The body is pressed with a teeming bore extending through it, and the exterior surfaces of the body are coated with a glaze forming frit. The frit coated body is then fired in an oxidizing furnace atmosphere at a temperature of 1000°C for about two hours, thereby sintering and densifying the body. The glazed surfaces are protected from the oxidizing atmosphere, but the

surfaces of the internal bore are unprotected, giving rise to an oxidized, carbon-depleted zone to a depth of 1-5 mm. The fired body is then submerged in a slip or slurry containing a fine carbon-free refractory powder, preferably alumina, in an organic/water vehicle. This is preferably placed under a vacuum for 15 minutes or more so as to remove entrapped oxygen from the oxidized zone, and then pressurized to cause the refractory-containing slurry to infiltrate the evacuated pores of the oxidized zone. The refractory body is then removed from the slurry and is subjected to a low temperature cure to volatilize and drive off the organic/water slurry vehicle. Since most nozzles are conventionally preheated prior to service, the latter curing step may be eliminated.

The purpose of forming an oxidized carbon-depleted zone in the bore of the nozzle or other body of US 5,370,370 and subsequently filling the created pores in this zone with the carbon-free refractory material, is to eliminate emissions of carbon monoxide gas from the bore, while retaining resistance to erosion and thermal shock by the molten steel flowing through the bore. The carbon is removed because it is thought that emission of carbon monoxide from the nozzle contributes to the deposition of alumina by the following reaction:



and the presence of carbon in the nozzle body is thought to contribute to the generation of carbon monoxide gas.

A problem associated with the process of forming a nozzle or other refractory body as disclosed in US 5,370,370, is that the step of infiltrating the pores of the carbon-depleted oxidized zone by means of the slurry of refractory material is laborious and time-consuming. However, it is clear from the teaching of US 5,370,370 that this step of re-filling the pores of the carbon-depleted zone with refractory material is necessary, and in fact is the heart of what the inventors of that patent regarded as their invention. For example, in column 5, lines 9-12 of the patent it is stated that elimination of the carbon bond phase and other carbon from

the refractory creates thermal shock problems, increased permeability and provides a reaction path for other oxidants to enter the melt. Once the pores have been infiltrated with the replacement refractory material, however, these problems are stated to be overcome.

The inventors of the present invention, however, have surprisingly found that, contrary to the teaching of US 5,370,370, it is generally not necessary to infiltrate the pores of a porous zone in a carbon-bonded refractory article with replacement refractory material in order to obtain an erosion-resistant, thermal shock resistant and anti-alumina build-up surface. In particular, the present inventors have found that a coating of glaze on a porous surface layer may provide excellent resistance to alumina deposition, and resistance to erosion and thermal shock.

According to a first aspect, therefore, the present invention provides an article for use with molten metal, comprising a body formed from carbon-bonded refractory material, a surface layer of the body being porous, characterised in that the porous surface layer has a coating of glaze.

The porous surface layer of the body preferably comprises only part of the external surface of the body. (By "external surface" is included surfaces of the body which define a bore or other internal cavity of the body.)

The fact that a glaze coating on a porous surface layer can provide the advantages referred to above is extremely surprising, not least in view of the teaching of US 5,370,370 that it is necessary to fill the pores with replacement refractory material (preferably alumina). While not wishing to be bound by any particular theory as to the reasons for the efficacy of the invention, the inventors nonetheless believe that the glaze (or constituents thereof) may react (for example during pre-heating and/or during use) with constituents of the refractory material of the article to cause the precipitation of reaction products which provide a substantially impervious and erosion-resistant surface layer.

The article according to the first aspect of the invention may, for example, comprise a nozzle or shroud for use in the casting of steel, the nozzle or shroud having a longitudinal bore. In such embodiments, the porous surface layer preferably comprises at least part of the surface layer of the bore of the nozzle or shroud. In some embodiments of the invention, substantially no surface of the nozzle or shroud other than the or each surface of the bore has a porous surface layer.

Additionally or alternatively, the nozzle or shroud (or other article according to the invention) has a top surface (i.e. a surface which comprises the top surface during normal use) at least partially, preferably entirely, formed from the porous surface layer. The top surface of the article is preferably a "slide plate", i.e. a surface which in use forms part of a sliding plate mechanism for placing the article in its operating position and subsequently removing it. (In a sliding plate mechanism, the slide plate of the article slides with respect to another slide plate of the mechanism with which it is in contact; the other slide plate may be fixed or it may itself be movable.)

The article according to the first aspect of the invention may alternatively (for example) comprise a stopper rod for use in the casting of steel, the porous surface layer preferably comprising at least part of a nose portion of the stopper rod. (By the "nose portion" is meant that portion of the stopper rod which is lowermost during use, and which cooperates with the outlet of a tundish or other vessel to control the flow of molten metal through the outlet.)

In preferred embodiments of the invention, at least a portion of the glaze coating permeates at least a portion of the porous surface layer. The amount of the glaze permeating the porous surface layer is preferably greatest at an outwardmost region of the layer and decreases with depth towards an inwardmost region of the layer.

The glaze may generally comprise substantially any suitable vitreous substance or composition. The glaze is preferably a high temperature glaze, i.e. it preferably has a melting point of at least 700 °C, more preferably at least 800 °C, even more preferably at least 1000 °C, especially at least 1200 °C. The melting point of the glaze is preferably no greater than 1500 °C, more preferably no greater than 1450 °C, especially no greater than 1400 °C, for example about 1300 °C.

In preferred embodiments of the invention, the glaze may comprise one or more of: silicon, silicon carbide, silica, colloidal silica, and silicate. Silicon is preferably present in the amount of at least 10 weight %, more preferably at least 15 weight %, even more preferably at least 18 weight %; preferably the silicon is present in the amount no more than 40 weight %, more preferably no more than 35 weight %, even more preferably no more than 30 weight %, especially no more than 27 weight %, for example approximately 20 or 25 weight %. Silicon carbide is preferably present in the amount of at least 2 weight %, more preferably at least 4 weight %, even more preferably at least 6 weight %; preferably the silicon carbide is present in the amount of no more than 10 weight %, more preferably no more than 9 weight %, for example approximately 8 weight %. Silicate is preferably present in the amount of at least 2 weight %, more preferably at least 4 weight %, even more preferably at least 7 weight %; the silicate is preferably present in the amount of no more than 60 weight %, more preferably no more than 40 weight %, even more preferably no more than 30 weight %, especially no more than 25 weight %. All percentages are based on the total weight of the glaze.

The glaze preferably includes aluminium, more preferably in the form of aluminium phosphate. Where present, the aluminium phosphate is preferably present in the amount of approximately 2 to 10 weight %, more preferably 3 to 8 weight %, for example approximately 5 weight %, based on the total weight of the glaze. In some embodiments of the invention, the glaze may include borax; in such embodiments, the borax is preferably present in the amount of at least 5 weight %, more preferably at least 8 weight %, even more preferably at least 12 weight %; preferably the borax is present in the amount of no more than 40 weight %, more

preferably no more than 30 weight %, especially no more than 25 weight %. One or more clays may be included in the glaze composition, for example Bentonite.

Where present, the clay is preferably in the amount of at least 0.25 weight %, more preferably at least 0.50 weight %; the clay is preferably present in the amount of no more than 5 weight %, more preferably no more than 3 weight %.

The porous surface layer is preferably carbon-depleted with respect to the remainder of the body of carbon-bonded refractory material. At least a portion of the porous surface layer is preferably substantially carbon-free. More preferably, the chemical composition of the porous surface layer is such that at least an inwardmost region of the layer includes carbon, and the proportion of carbon in the layer decreases towards an outwardmost region of the layer. Most preferably, at least the outwardmost region of the porous surface layer is substantially carbon-free.

The depth of the porous surface layer is preferably at least 0.2 mm, more preferably at least 0.4 mm, even more preferably at least 0.6 mm, especially at least 0.8 mm. The porous surface layer has a depth of preferably no greater than 5.0 mm, more preferably no greater than 4.0 mm, even more preferably no greater than 3.0 mm, especially no greater than 2.0 mm, for example about 1.0 mm. The porous surface layer is preferably substantially carbon free to a depth of at least 0.2 mm, more preferably at least 0.4 mm; it may, for example, be substantially carbon free to about half of the depth of the entire porous surface layer.

It will be appreciated that the boundary between the porous surface layer and the substantially non-porous region below it, will generally not be sharp; there will normally be a gradual transition from porosity to substantial non-porosity.

The carbon-bonded refractory material preferably comprises one or more metal oxides, e.g. alumina, magnesia and/or zirconia; it preferably further comprises graphite. The carbon bond is preferably formed by means of resin or pitch which is decomposed during firing.

It was mentioned above that some embodiments of the invention include a slide plate surface which is at least partially (preferably entirely) formed from the porous surface layer. The present inventors have found that conventional slide plates formed from carbon bonded refractory materials may sometimes become weakened due to loss of carbon during pre-heating or during use. The inventors have found that, by using the carbon-depleted porous surface layer of the invention for the surface of the slide plate, the slide plate is provided with a hard wearing surface which does not become weakened during pre-heat or during use because carbon loss is not an issue. In a sense, the carbon is "pre-depleted", thereby avoiding carbon loss during use which would weaken the material.

According to a second aspect, the invention provides a method of making an article according to the first aspect of the invention, comprising:

- (a) forming the body of carbon-bonded refractory material;
- (b) firing the body in an oxidizing atmosphere, thereby forming the porous surface layer by oxidative removal of carbon from the surface layer (oxidative firing); and
- (c) coating the porous surface layer with the glaze.

The oxidative firing step is preferably carried out in air or an alternative oxygen-containing atmosphere. The temperature of oxidative firing is preferably in the range 700 -1100 °C, more preferably 800 - 1000 °C, and most preferably the peak temperature is approximately 900 °C. The duration of oxidative firing is preferably at least 20 minutes, more preferably at least 30 minutes. Preferably the oxidative firing step is completed after no more than 1 hour, more preferably no more than 50 minutes, for example about 40 minutes.

The glaze coating step preferably comprises dip-coating, but other coating methods, for example spraying or painting, may be used. The method of the invention preferably further comprises the step of firing the body of carbon-bonded refractory material in a non-oxidising atmosphere (i.e. "non-oxidative firing") prior to firing it in an oxidizing atmosphere. The non-oxidative firing may be carried out in

an inert atmosphere, for example of nitrogen or argon gas, but it is preferably carried out in a reducing atmosphere, for example of carbon monoxide gas. The temperature of non-oxidative firing is preferably in the range 700 - 1100 °C, more preferably 800 - 1000 °C, and most preferably the peak temperature is approximately 900 °C. The duration of non-oxidative firing is preferably at least 40 minutes, more preferably at least 50 minutes. Preferably the non-oxidative firing step is completed after no more than 90 minutes, more preferably no more than 70 minutes, for example about 60 minutes.

The glaze coating step may in fact comprise two or more coating steps. In particularly preferred embodiments of the invention, two different glaze compositions are sequentially coated on the refractory article. Examples of preferred glaze compositions are as follows:

Example 1 - First Glaze Coating

<u>Component</u>	<u>Percentage By Weight</u>
aluminium phosphate	5 %
borax	25 %
silicon	25 %
silicon carbide	8 %
aluminosilicate	8 %
silica	5 %
carriers, binders, rheological control agents	balance

Example 2 - Second Glaze Coating

<u>Component</u>	<u>Percentage By Weight</u>
aluminium phosphate	5 %
silicon	20 %
silicon carbide	8 %
aluminosilicate	25 %
calcium metasilicate (Wollastonite)	5 %
silica	5 %

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clay	1 %
carriers, binders, rheological control agents	balance

All percentages are expressed as a percentage of the entire weight of the glaze.

The method preferably further comprises the step, prior to the oxidative firing and subsequent to the non-oxidative firing (for embodiments of the invention in which this is carried out), of applying to part of the body of carbon-bonded refractory material a substance which prevents that part of the body being oxidised during the oxidative firing. For example, for embodiments of the invention in which the article comprises a nozzle or shroud, all of the surfaces of the carbon-bonded body of the article except for all or part of the bore of the nozzle or shroud may be coated with the oxidation-preventing substance, in order to form the porous layer in the bore.

The oxidation-preventing substance preferably comprises a glaze. The oxidation-preventing glaze is preferably different to that which coats the porous surface layer. The oxidation-preventing substance preferably includes Borax. Other preferred constituents include: silicon and/or silicon carbide and/or aluminium phosphate.

The article according to the invention (e.g. a nozzle, shroud or stopper rod) may be formed from two or more different carbon bonded refractory materials. For example, the part or parts of the article which have a porous surface layer according to the invention may be formed from a different carbon bonded refractory material to that of the remainder of the article. For example, types or proportions of metal oxides (e.g. alumina, magnesia and/or zirconia) may be different in the different materials. The skilled person will be able to choose the appropriate materials for each particular application. The different carbon bonded refractory materials are preferably co-pressed during a conventional isostatic pressing process.

The invention will now be described, by way of example, with reference to the accompanying drawings, of which:

Figure 1 shows a submerged entry shroud according to the invention; and
Figure 2 shows an alternative submerged entry shroud according to the invention.

Figure 1 shows a submerged entry shroud 1, comprising a body 3 formed from carbon-bonded refractory material 4. The body 3 has a longitudinal bore 5 extending from an open upper end 7 to a lower end 9 which is blind. There are two outlets 11 at the lower end 9 of the longitudinal bore, the outlets extending laterally with respect to the axis of the bore, and inclined slightly downwards towards their open ends 13. The shroud has a conventional shape which is familiar to persons skilled in the art.

The longitudinal bore 5, including the blind lower end 9, has a porous surface layer 15 which has a coating layer of glaze 17, in accordance with the invention. In fact, the entire body 3 of carbon-bonded refractory material has a coating of the glaze 17, since the glaze coating has been formed by dipping the entire body into a vat of the glaze, but only the part of the glaze coating on the porous surface layer is shown, for clarity.

Figure 2 shows a submerged entry shroud 19 having a similar overall shape to that shown in Figure 1. The figure comprises complete (a) and partial (b) longitudinal cross-sectional views of the shroud, and a plan view (c) of the top of the shroud. The shroud is formed from three different carbon bonded refractory materials, identified by numerals 21, 23 and 25. Materials 21 and 25 are conventional, material 21 being a standard carbon bonded refractory material conventionally used to form the body of a submerged entry shroud, and material 25 being a standard slag-resistant carbon bonded refractory material which is situated on the outer surface of the shroud in the region of the shroud which will be in contact with the slag line during use.

Material 23 comprises a carbon bonded refractory material including a porous surface layer in accordance with the invention. This surface layer forms the slide plate surface of the shroud.

Claims

1. An article for use with molten metal, comprising a body formed from carbon-bonded refractory material, a surface layer of the body being porous, characterised in that the porous surface layer has a coating of glaze.
2. An article according to Claim 1, in which at least a portion of the glaze coating permeates at least a portion of the porous surface layer.
3. An article according to Claim 2, in which the amount of the glaze permeating the porous surface layer is greatest at an outwardmost region of the layer and decreases with depth towards an inwardmost region of the layer.
4. An article according to any preceding claim, in which at least a portion of the porous surface layer is substantially carbon-free.
5. An article according to any preceding claim, in which the chemical composition of the porous surface layer is such that at least an inwardmost region of the layer includes carbon, and the proportion of carbon in the layer decreases towards an outwardmost region of the layer.
6. An article according to Claim 5 when dependent upon Claim 4, in which at least the outwardmost region of the porous surface layer is substantially carbon-free.
7. An article according to any preceding claim, in which the glaze has a melting point of at least 700 °C.
8. An article according to any preceding claim, in which the glaze has a melting point of no greater than 1500 °C.

9. An article according to any preceding claim, in which the glaze comprises one or more of: silica, silicon carbide, and colloidal silica.
10. An article according to any preceding claim, in which the glaze comprises aluminium, preferably in the form of aluminium phosphate.
11. An article according to any preceding claim, in which the glaze comprises one or more clays, for example Wollastonite.
12. An article according to any preceding claim, in which the porous surface layer of the body comprises only part of the external surface of the body.
13. An article according to any preceding claim, comprising a nozzle or shroud for use in the casting of steel, the nozzle or shroud having a longitudinal bore.
14. An article according to Claim 13 when dependent upon Claim 12, in which the porous surface layer comprises at least part of the surface layer of the bore of the nozzle or shroud.
15. An article according to any preceding claim, including a slide plate, the porous surface layer of the body comprising at least part of the surface layer of the slide plate.
16. An article according to anyone of claims 1 to 12, comprising a stopper rod for use in the casting of steel, the porous surface layer preferably comprising at least part of a nose portion of the stopper rod.
17. A method of making an article according to any preceding claim, comprising:
 - (a) forming the body of carbon-bonded refractory material;
 - (b) firing the body in an oxidising atmosphere, thereby forming the porous surface layer by oxidative removal of carbon from the surface layer (oxidative firing);and

(c) coating the porous surface layer with the glaze.

18. A method according to Claim 17, further comprising the step of firing the body of carbon-bonded refractory material in a non-oxidising atmosphere (non-oxidative firing) prior to firing it in an oxidizing atmosphere.

19. A method according to Claim 17 or Claim 18, further comprising the step, prior to the oxidative firing and subsequent to the non-oxidative firing (if this is done), of applying to part of the body of carbon-bonded refractory material a substance which prevents that part of the body being oxidised during the oxidative firing.

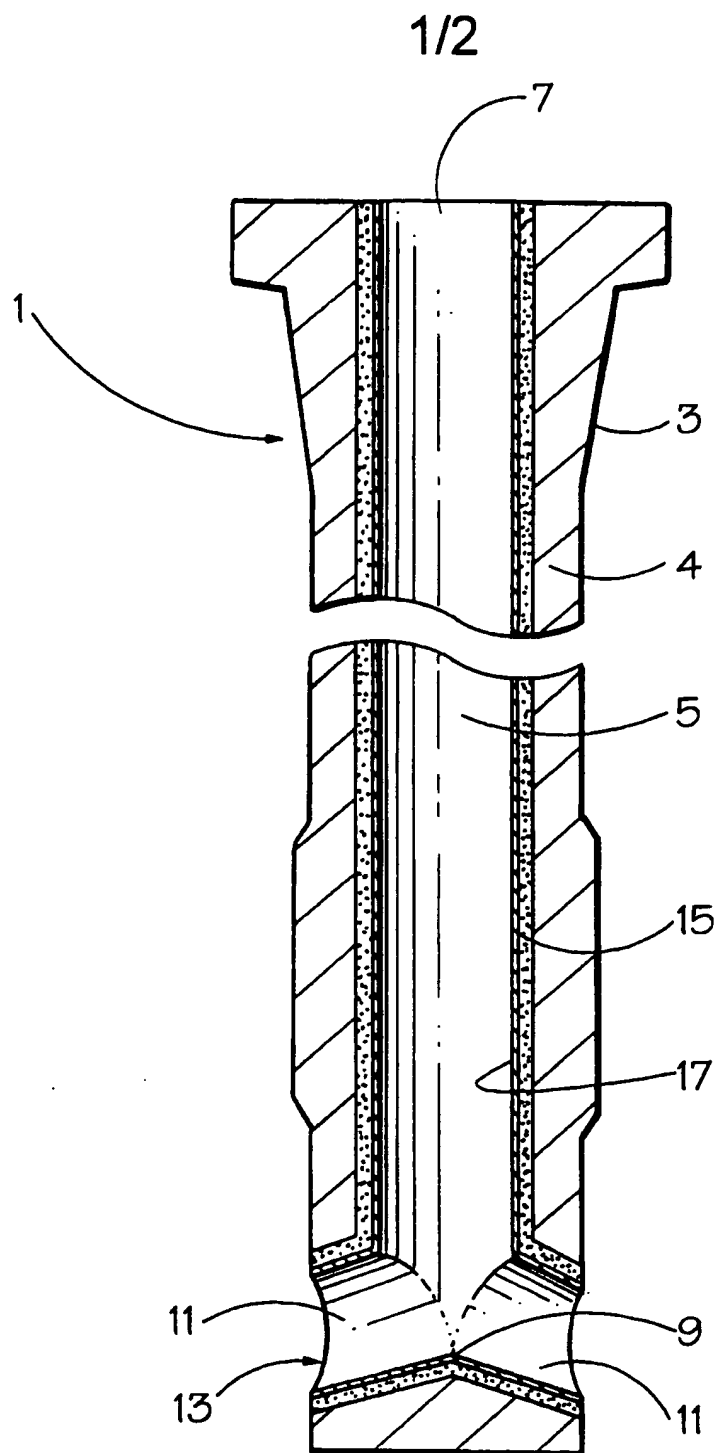


FIG.1.

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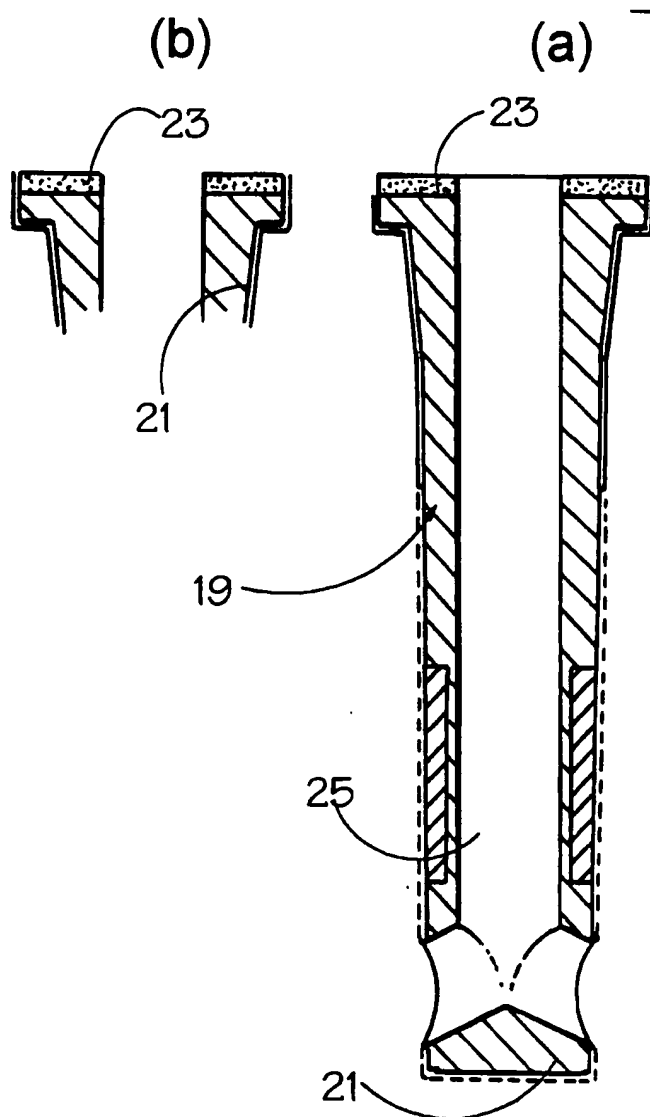
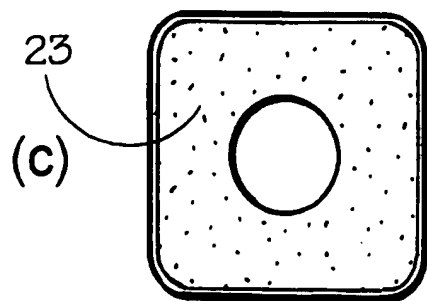


FIG.2.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/02194

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B22D41/54 B22D41/18 B22D41/32 C04B41/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B22D C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 370 370 A (BENSON PAUL M) 6 December 1994 (1994-12-06) cited in the application column 5, line 57 -column 8, line 23; figure ---	1,3-5,9, 13,14
A	EP 0 296 981 A (VESUVIUS CRUCIBLE CO) 28 December 1988 (1988-12-28) abstract; claims 1-17 ---	1,9, 12-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/02194

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 681 499 A (HANSE ERIC ET AL) 28 October 1997 (1997-10-28) claims 1-25; figures 1-8 ---	1,2,4, 13-19
A	US 5 714 244 A (REY JACQUES ET AL) 3 February 1998 (1998-02-03) figure 1 -----	1-19

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Information on patent family members

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